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MEMORANDUM FOR IN-HOUSE PUBLICATIONS

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Jeff Sheehy "Theoretical Investigations of HEDM" **HEDM Conference Presentation (Statement A)**

Theoretical Investigations of HEDM

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Present HEDM Theory and Computations

- Structure, stability, and spectroscopy of prototype HEDM-doped cryogenic matrices
  - ⇒ Spectral theory of chemical binding
  - ⇒ Applications to sodium- and aluminum doped rare-gas clusters and solids: $NaAr_n$, $AlAr_n$

- Structure, stability, and spectroscopy of candidate cryogenic HEDM dopant species
  - ⇒ Characterization of argon matrices seeded with small boron-carbon and pure carbon molecules: B_xC_y, $x,y = 1\text{-}6$; C_n, $n = 1\text{-}12$

- Properties of non-cryogenic new propellants and additives
  - ⇒ Structures, spectra, and heats of formation for various newly synthesized and proposed fuels, oxidizers, and monopropellants: $[(N_3)_3C]^+$, $[NCNNO_2]^-$, $C_5H_8O_2$, $C_{17}H_{24}N_4O_8$

Potential-Energy Surfaces

- Spectral theory of chemical binding aims to provide accurate electronic potential-energy surfaces for aggregates of interacting atomic or molecular species

  - ⇒ Provides a unified treatment of all types of physical and chemical binding
  - ⇒ Gives a new foundation for a class of theories (AIM and DIM) that build potential surfaces from information related to component fragments
  - ⇒ Diatomic-molecule calculations are the most demanding requirement from conventional quantum chemistry, and can be done once and for all
  - ⇒ Potentially applicable to large systems (10^3 atoms)

- Accurate potential-energy surfaces yield information about structures, spectroscopy, stability, and reactivities of chemical systems

Diatomic-Molecule Calculations

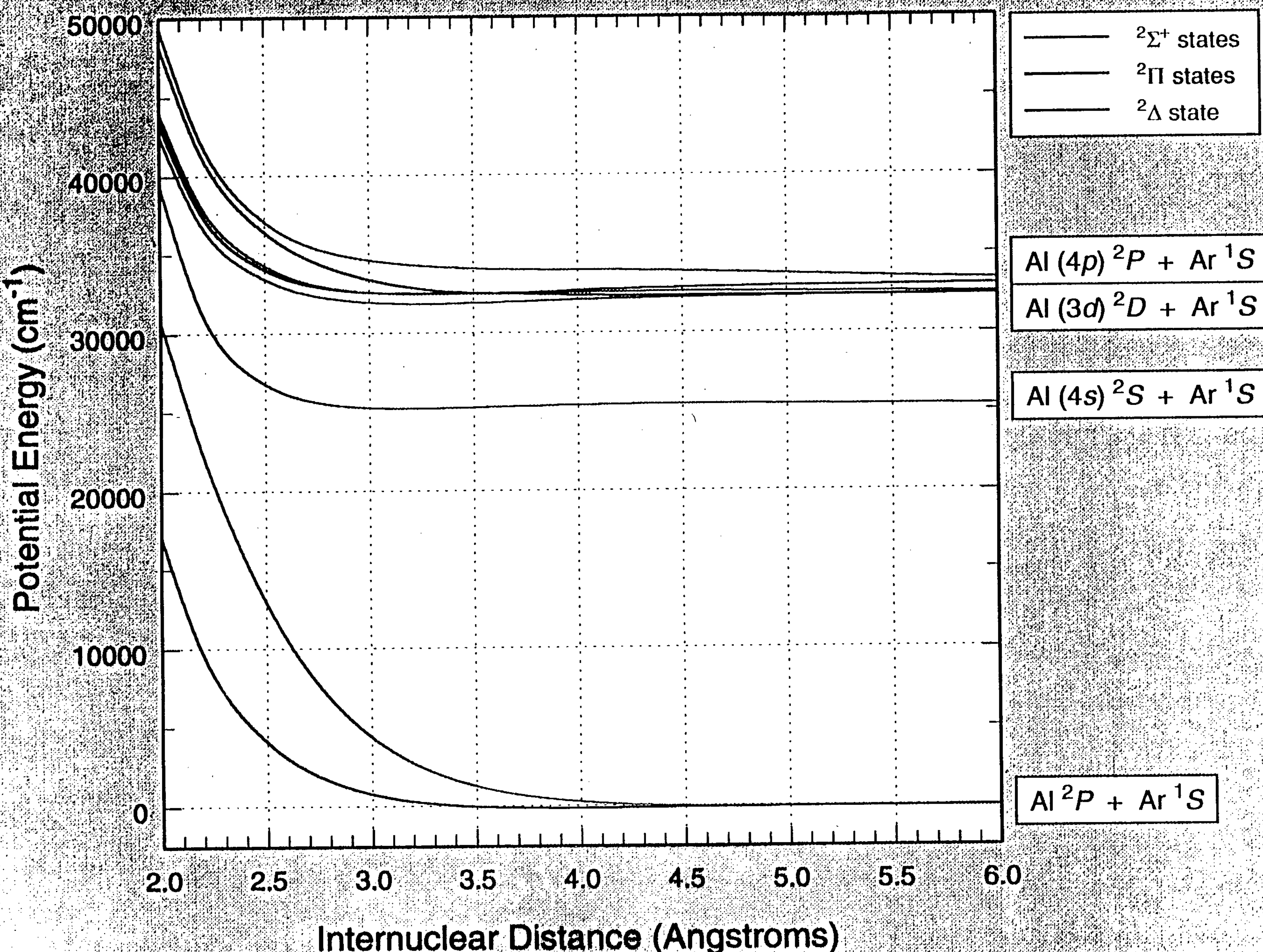
- Due to the availability of experimental data from Mario Fajardo and others, alkali atoms in rare-gas matrices are studied as a prototype of atom-seeded solid H_2

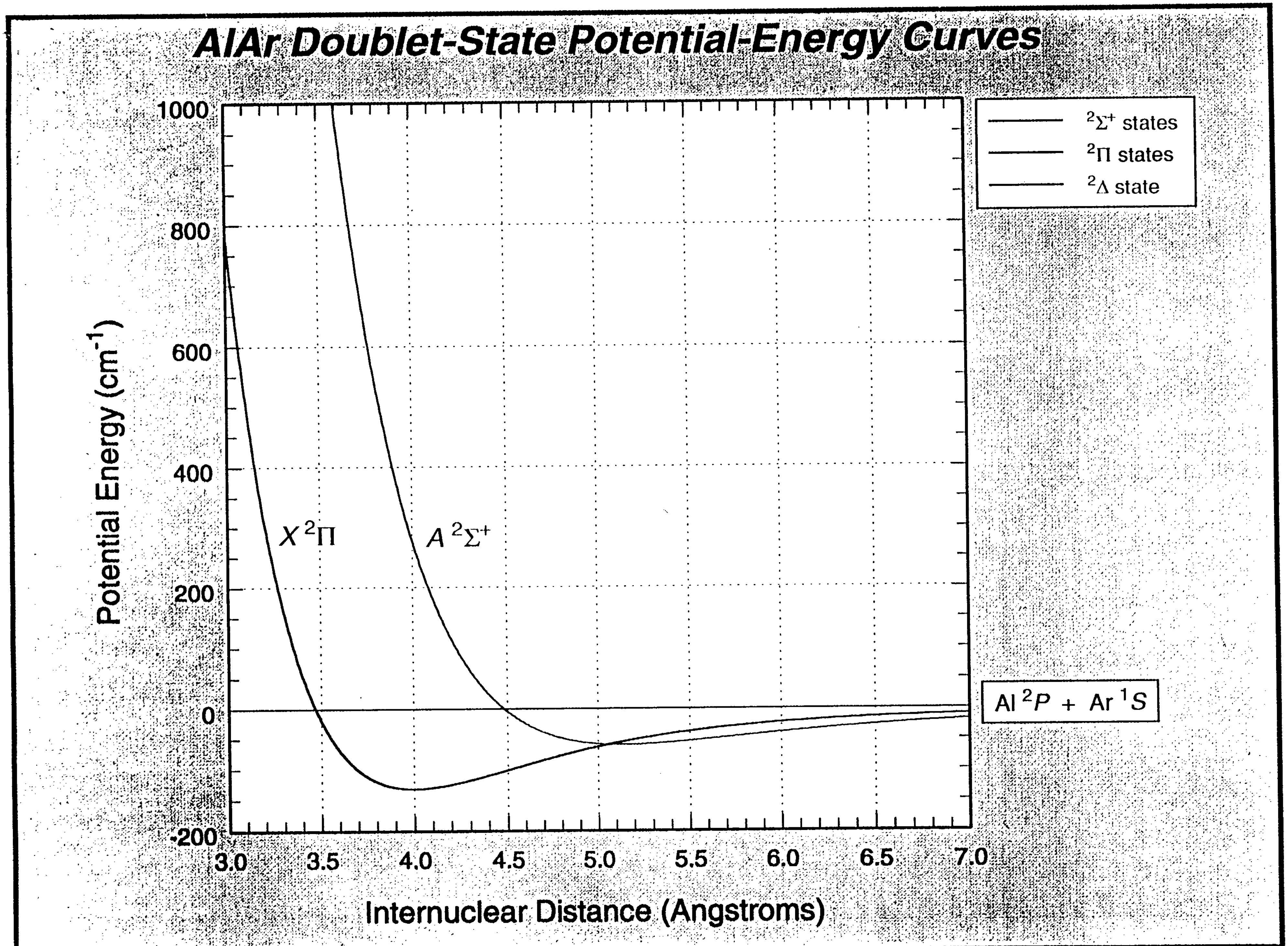
- Potential-energy, dipole-moment, and transition-moment functions for the ground and lowest nine excited states of NaAr are calculated employing CASSCF/MRCI and EA-EOM-CC methodologies; lowest states are benchmarked using CCSD(T)

- Similar calculations for AlAr are in progress; preliminary results obtained employing CASSCF(0.05)/MRCI are available

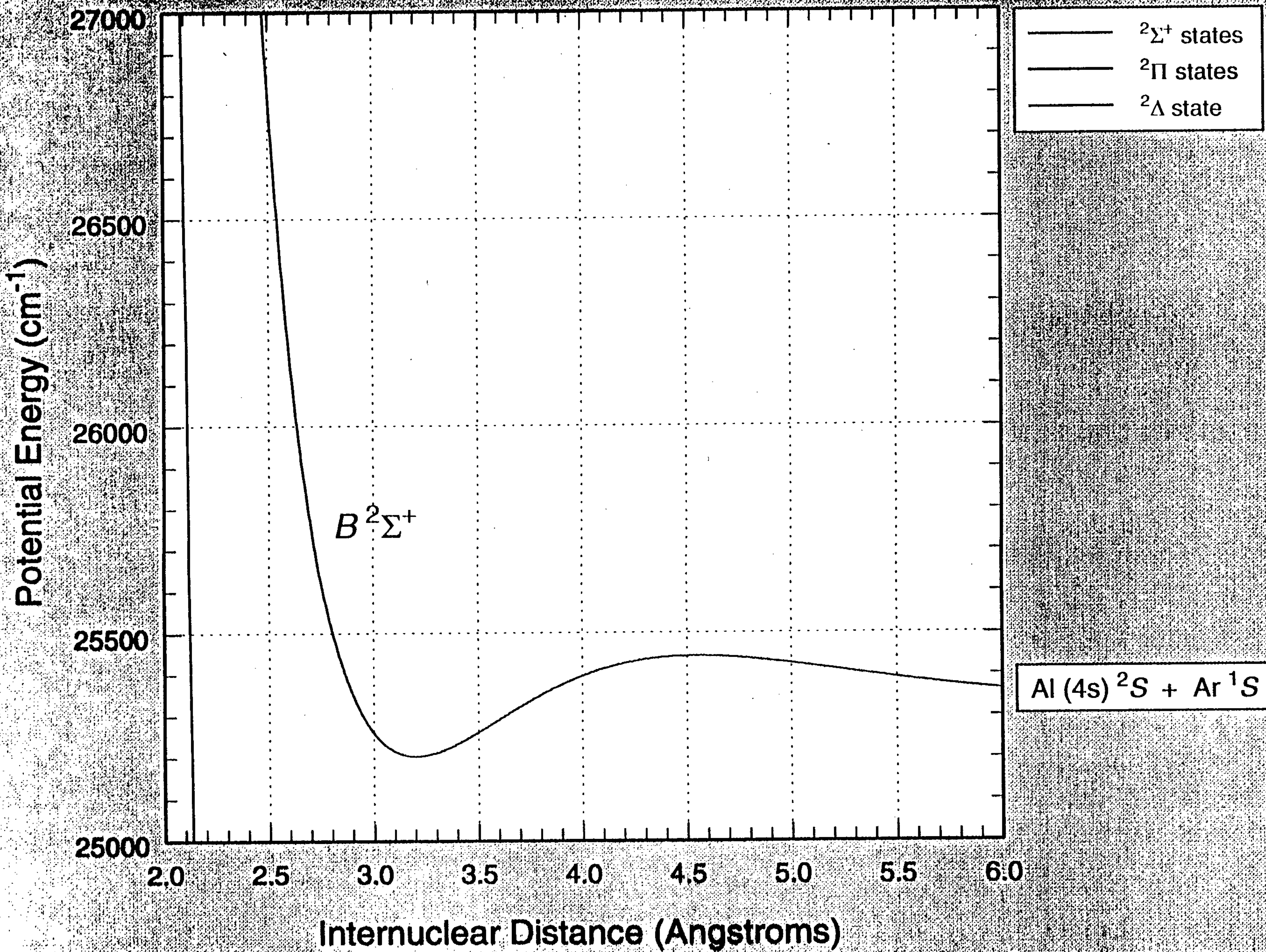
- Data so obtained are used directly in computational implementations of the spectral theory and in ensuing cluster simulations ($NaAr_n$, $AlAr_n$)

AlAr Doublet-State Potential-Energy Curves

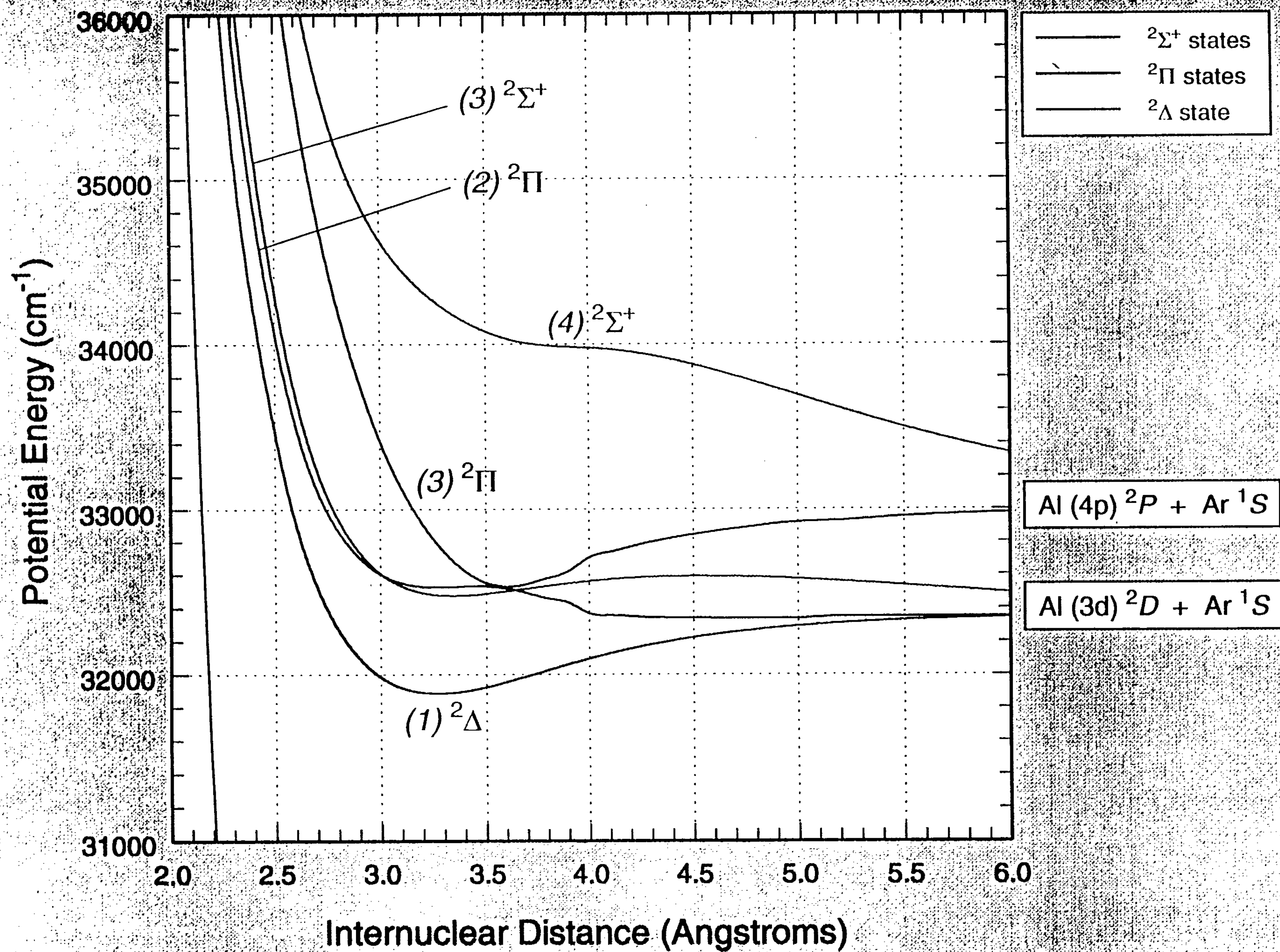



AlAr Doublet-State Potential-Energy Curves
Potential Energy (cm^{-1})
1000
800
600
400
200
0
-200
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
Internuclear Distance (Angstroms)
$^2\Sigma^+$ states
$^2\Pi$ states
$^2\Delta$ state
$X\,^2\Pi$
$A\,^2\Sigma^+$
Al ^2P + Ar ^1S

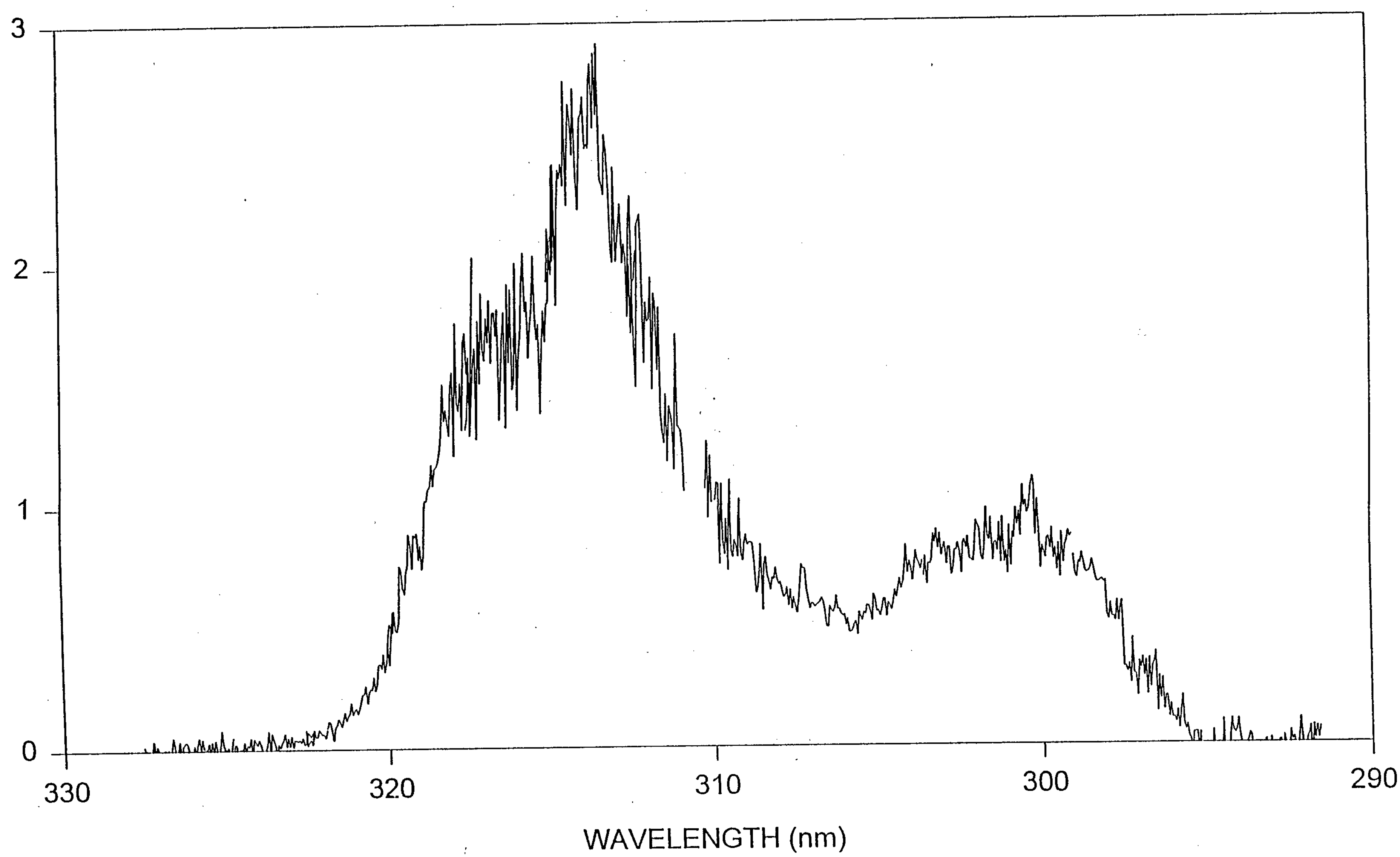
AlAr Doublet Excited-State Potential-Energy Curves



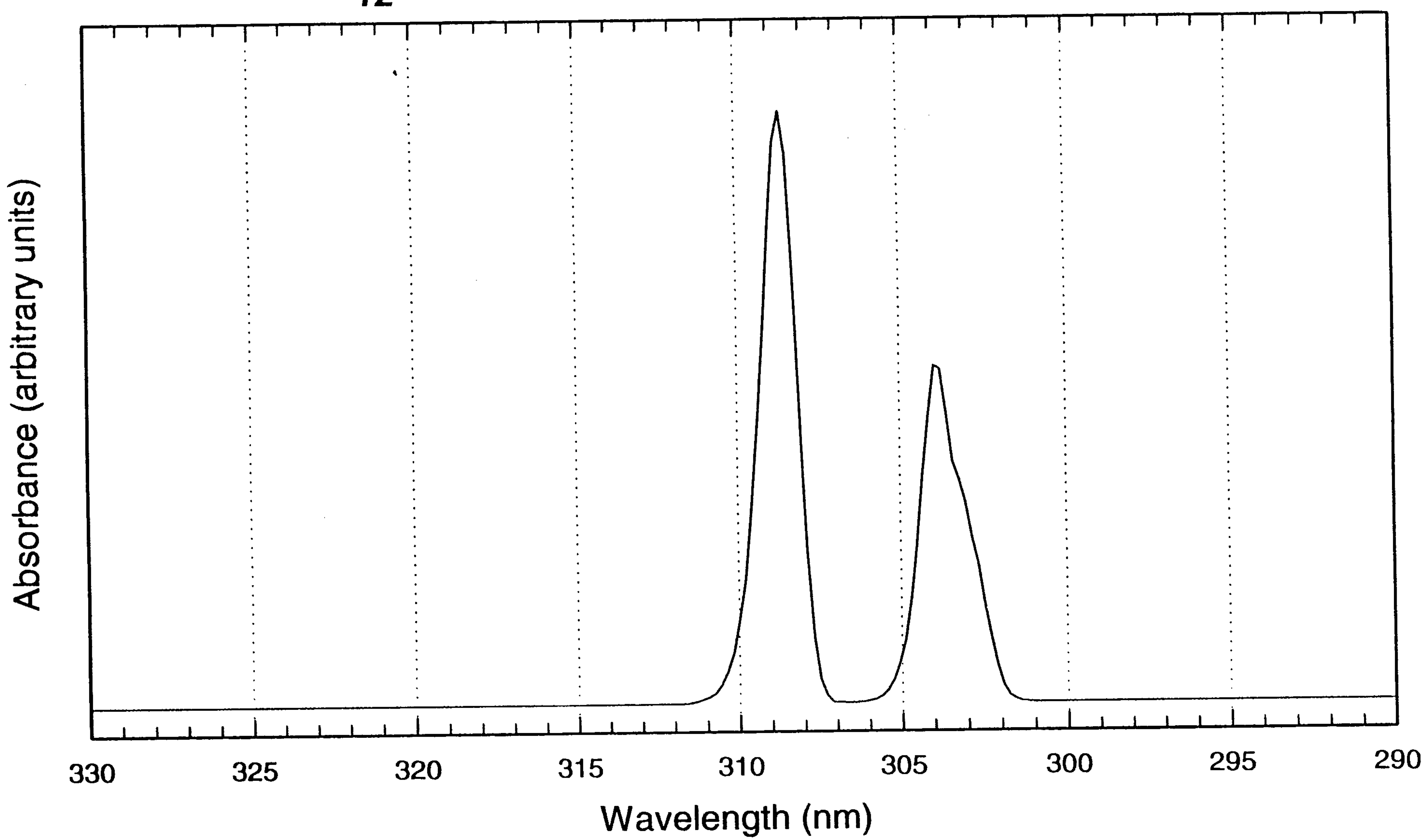
AlAr Doublet Excited-State Potential-Energy Curves



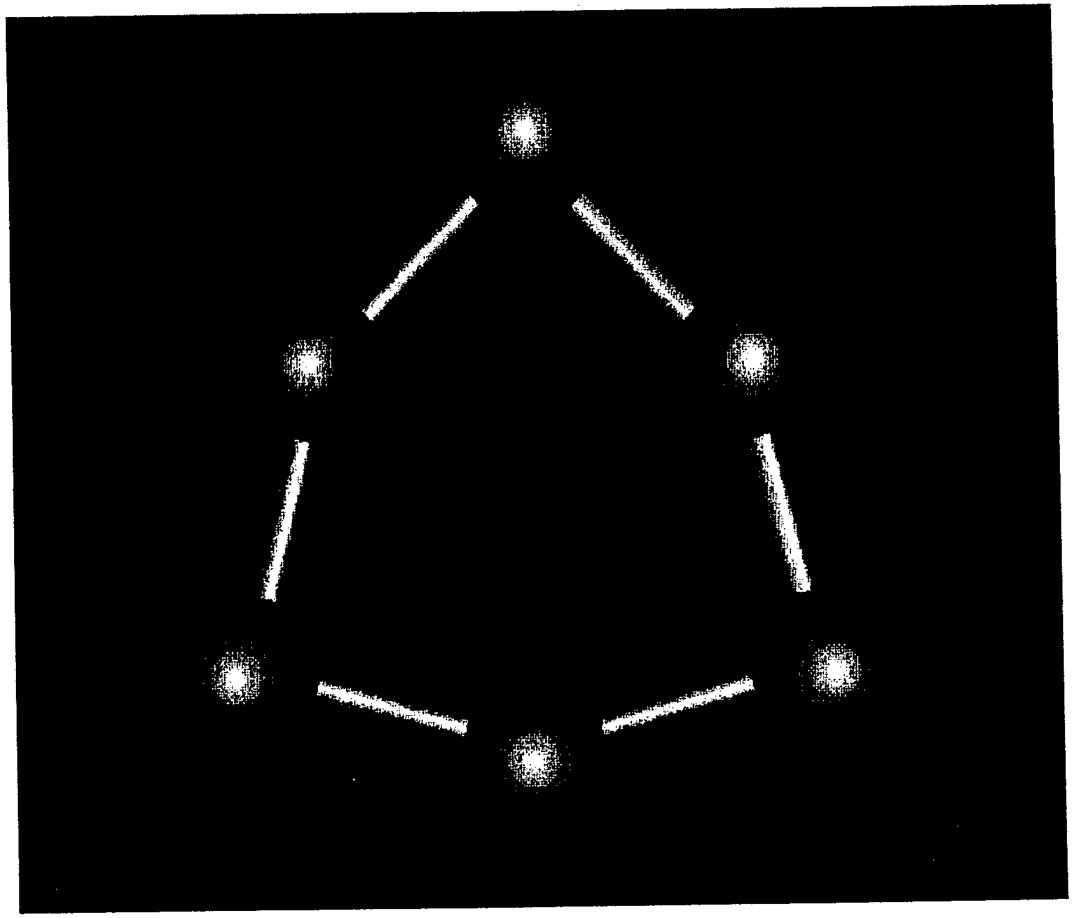
$AlAr_{12}$



$AlAr_{12}$ Absorption Spectrum at $T = 30$ K



Identification of Cyclic C_6 in Argon Matrix

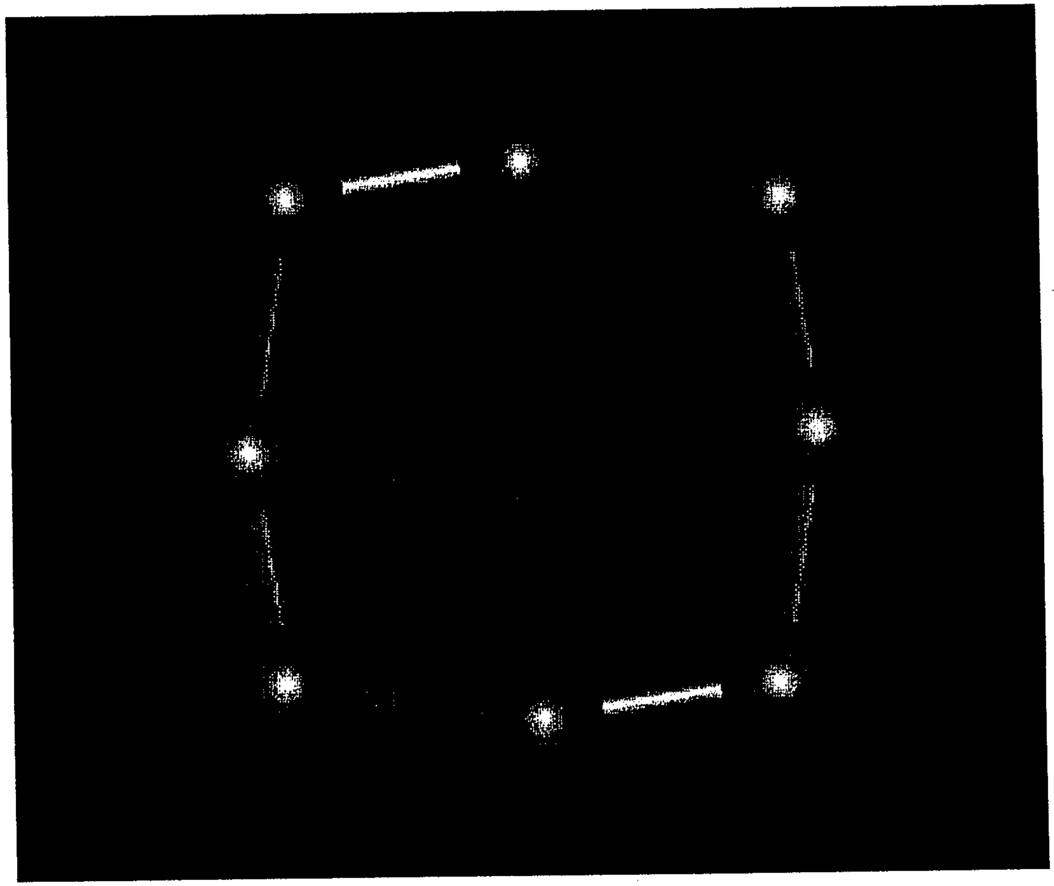


- CCSD(T)/cc-pVDZ ground-state equilibrium structure (D_{3h} symmetry)
- First identification of a neutral small cyclic polycarbon

Vibrational Frequencies and Intensities of Cyclic C_6

Mode	B3LYP/cc-pVDZ	CCSD(T)/cc-pVDZ	Literature
$\nu_1(a_1')$	1222	1183	1183
$\nu_2(a_1')$	659	556	556
$\nu_3(a_2')$	1437	1371	1371
$\nu_4(e')$	1769 (404)	1736 (420)	1768
$\nu_5(e')$	1219 (1)	1178(1)	1222
$\nu_6(e')$	633 (25)	576 (43)	337
$\nu_7(a_2'')$	419 (8)	380 (7)	380
$\nu_8(e'')$	519	492	492

Identification of Cyclic C_8 in Argon Matrix



- B3LYP/cc-pVDZ ground-state equilibrium structure (C_{4h} symmetry)
- Identified for the first time in the argon matrices containing cyclic C_6 and various other linear and cyclic C_n compounds ($n = 3,4,\ldots,12$)

Approach To Propellant Ingredient Modeling

- Employ various methods to solve the molecular electronic Schrodinger equation from quantum mechanics:

- Potential energy surfaces -- energy profiles associated with all possible arrangements of the atoms in a chemical system -- yield synthetic routes and decomposition pathways

- Structures and certain spectra (*e.g.*, IR) are obtained from evaluating derivatives of the energy with respect to nuclear coordinates

- Other properties, (*e.g.*, NMR spectra) are obtained from evaluating energy derivatives with respect to other quantities (*e.g.*, magnetic field)

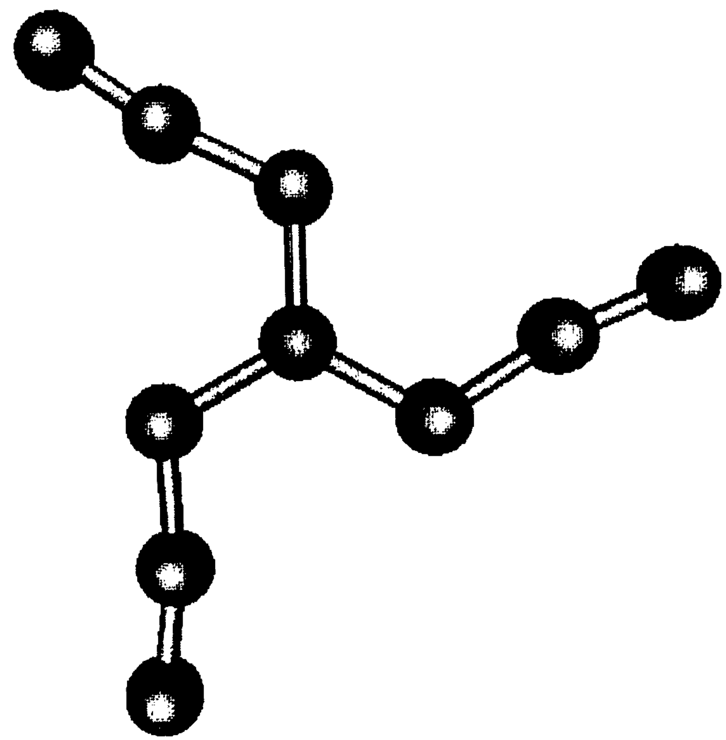
- Thermodynamic properties obtained from relative energetics of reactants, intermediates, and product species

Payoffs From Propellant Ingredient Modeling

Several benefits to propellant synthesis programs are derived from theory and modeling work:

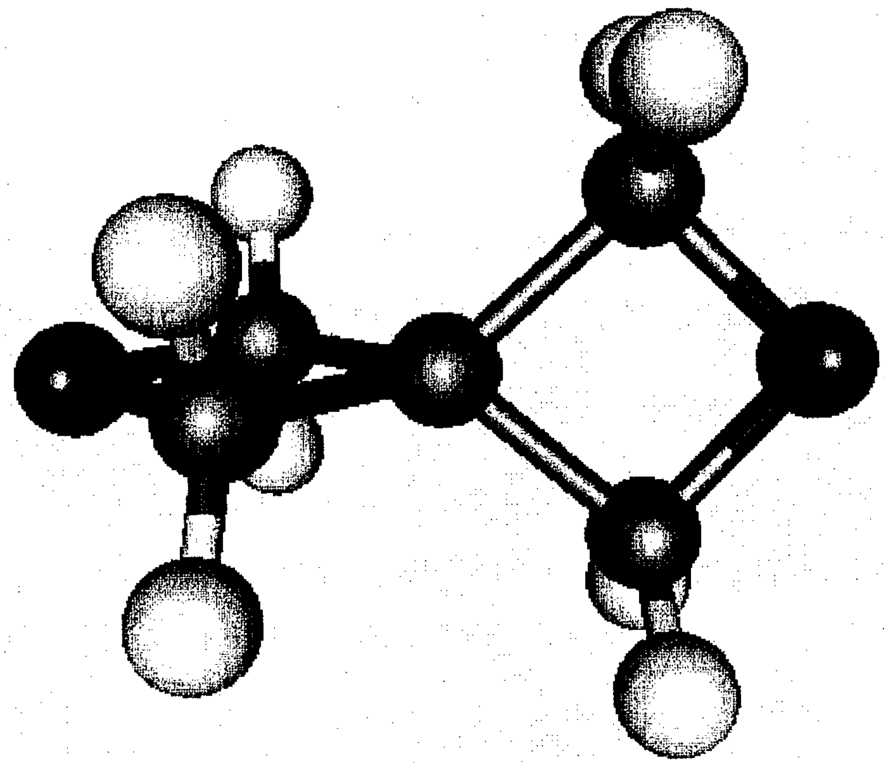
- Focus laboratory efforts by predicting characteristics of candidates
  - ⇒ Stabilities
  - ⇒ Energy content
  - ⇒ Propellant performance
- Reduce the number of experiments required to synthesize candidates
  - ⇒ Suggest synthetic routes
  - ⇒ Eliminate "blind alleys" and "dead ends"
- Aid in identification of unknown molecules
  - ⇒ Calculate properties (*e.g.*, spectra) for comparison with measurements
- Generally substitute relatively inexpensive modeling for comparatively expensive laboratory work

Triazidocarbenium Cation



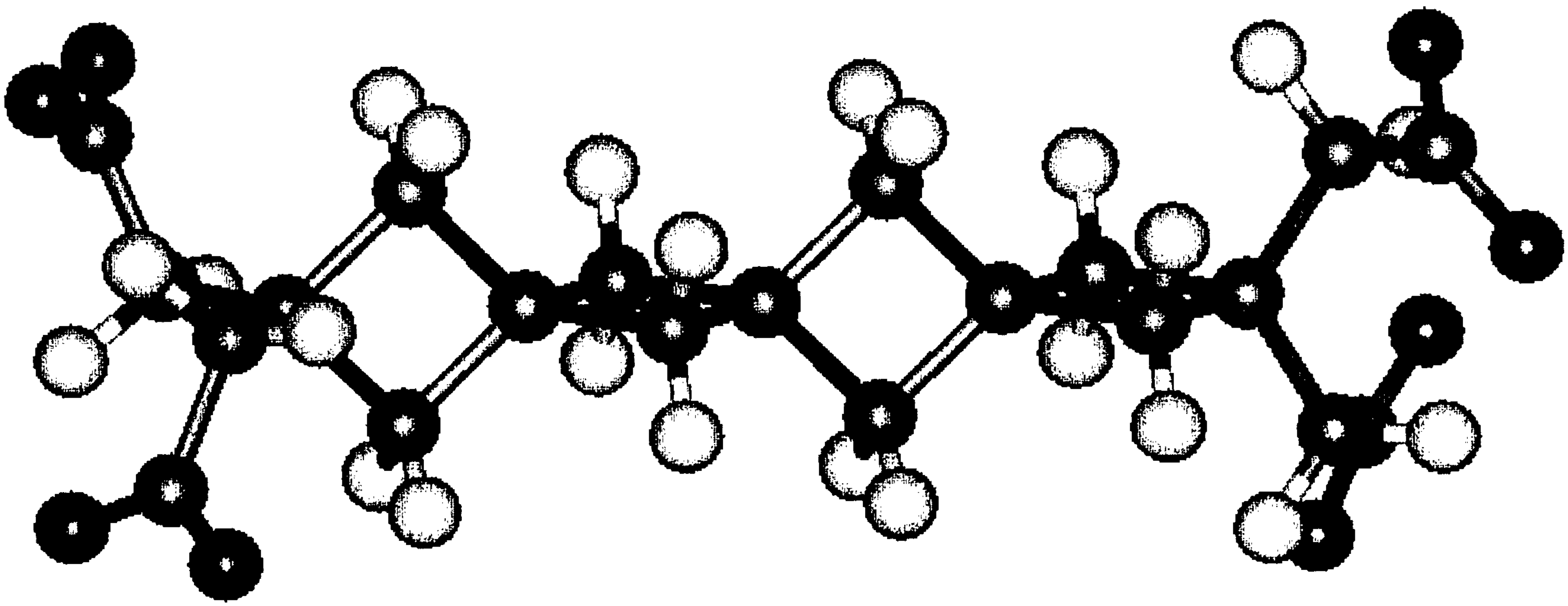
- Energetic cation for dinitramide or perchlorate salts
- Computed infrared, Raman, and NMR spectra
- Heat of formation of $[(N_3)_3C]^+ [N(NO_2)_2]^-$ is +252 kcal/mol

2,6-dioxaspiro[3.3]heptane



- Partially oxidized “hydrocarbon” fuel
- ΔH_f = - 30.2 kcal/mol; Isp (neat with LOX) = 296 sec

Tetra(nitromethyl)spirotriskadecane



- Calculations on thermodynamic properties of this molecule are in progress

Summary

- All aspects of the research and development program in new propellant ingredients at AFRL are supported by theory and modeling

- The theory and modeling effort serves to limit the number of experiments that must be carried out through substantial screening of target systems, providing efficiency and cost savings to the program

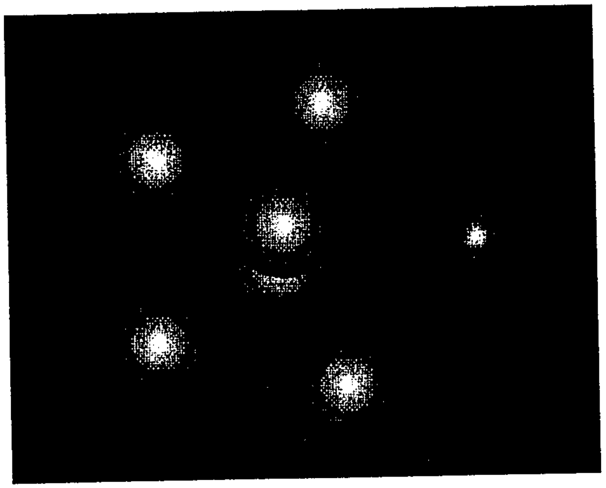
- The interaction between theoreticians and experimenters facilitates the accomplishment of program goals that could not otherwise be accomplished

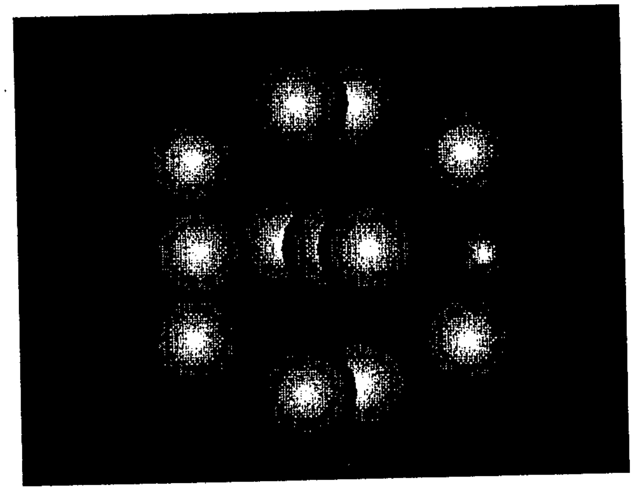
- Theory and modeling provides vital directional signposts along the road to developing new energetic propellants, which are essential to meeting several IHPRPT performance objectives

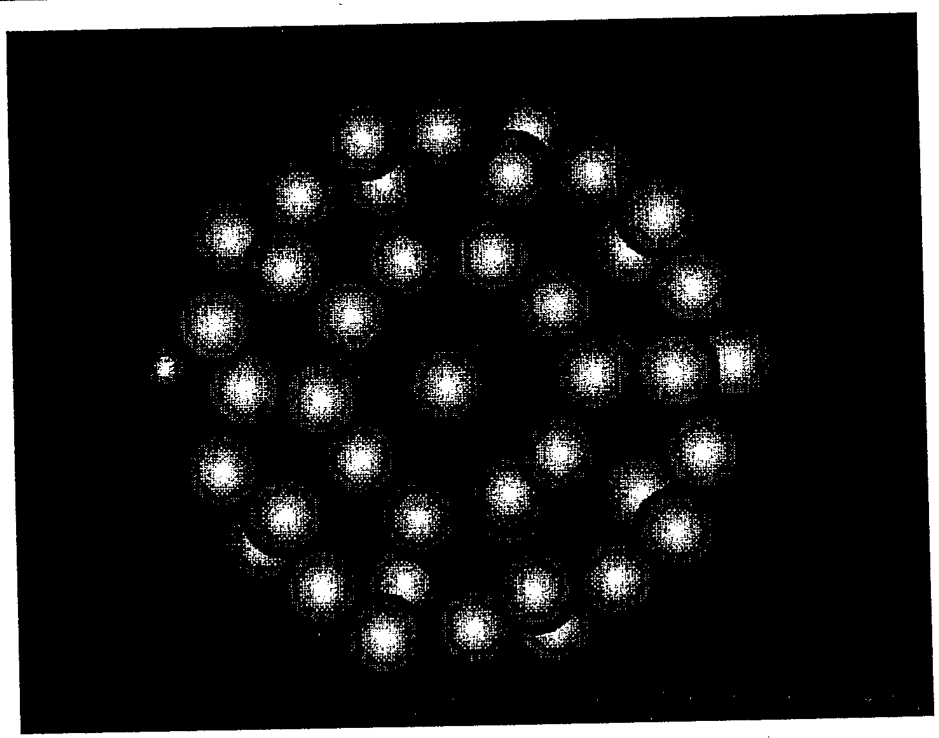
Theory and Computations in Propellants Research

Area of Interest	Type of Model	Impact of Modeling	Applications
Synthesis of new propellant ingredients	Calculations of stationary points on potential surfaces	Exploration of efficient synthetic routes and dissociation pathways	Cubane (C_8H_8), pentaprismane ($C_{10}H_{10}$)
Stabilities of proposed and synthesized new propellants	Calculations of structures, spectra, properties	Effective screening of proposed compounds; determine which merit experimental study	$[(N3)C]^+$, $[NCNNO2]^-$, $C_5H_8O_2$, $C_{17}H_{24}N_4O_8$
Discovery and characterization of new cryogenic HEDM additives	Calculations of infrared frequencies and intensities; spectral modeling	Predict whether candidate molecules can be isolated; aid in data analysis	Li_xB_y, Li_xC_y, Si_xC_y ($x,y = 1,2,3$); cyclic C_6 and C_8
Characterization of doped cryogenic solid propellants	Spectral theory of chemical binding in conjunction with molecular dynamics simulations	Predict structures, densities, dopant concentrations, and stabilities of cryogenic HEDM propellants	Na/Ar_n, Al/Ar_n (prototypes); Li/H_2, B/H_2, LiB/H_2, $B/H_2/He_{(l)}$

Snapshots of $AlAr_n$ Clusters







Application to Aluminum-Argon Clusters

- Structures and absorption spectra of $Al(Ar)_n$ clusters with $n = 1, 6, 12,$ and 54 have been studied; results are compared with data from Mitchio Okumura (Caltech).

- Simulations employ Metropolis Monte-Carlo method combined with a generalized Balling and Wright or spectral theory treatment of the potential functions

- Makes use of AlAr diatomic potential-energy, dipole-moment, and transition-moment functions involving all states of spectroscopic interest (generalized Balling and Wright) or all states calculated (spectral theory)

- Analogous studies of $NaAr_n$ clusters and solids are in progress, utilizing the new potential curves and recent developments in implementation of the spectral theory